

Influence of H⁺ and Cl⁻ Ions on Inhibitive Performance of Poly(aniline) for Iron Corrosion in Acid

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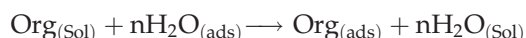
ABSTRACT: The inhibition effect of poly(aniline) on pure iron corrosion in 1M HCl and with various H⁺ ions and Cl⁻ ions concentrations was investigated by the polarization and electrochemical impedance spectroscopy methods. The results showed that poly(aniline) suppressed both cathodic and anodic processes of iron dissolution in 1M HCl by its adsorption on the iron surface according to Langmuir's adsorption isotherm. The inhibition efficiency of poly(aniline) was found to increase with the inhibitor concentrations. Further, it was observed that, there was no significant variation in corrosion potential (E_{corr}) values in the presence of inhibitors suggesting that, this polymer

behaved as mixed type inhibitor. Similar studies for the inhibitor at 500 ppm in various concentrations of H⁺ and Cl⁻ ions, have shown that the inhibition efficiency decreases with decrease in concentrations of H⁺ ions and Cl⁻ ions in aqueous solution. It reveals that, the adsorption of inhibitor on iron surface is by more cationic form of inhibitor and higher efficiency at higher H⁺ and Cl⁻ ions is due to enhanced adsorption of cat ionic form of inhibitor molecules. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3988–3993, 2007

Key words: poly(aniline); inhibition; corrosion; iron; HCl

INTRODUCTION

The investigation of the inhibition of corrosion of iron is a matter of high theoretical as well as practical interest.¹ Acids find many applications in many operations such as pickling, cleaning, descaling, etc. Because of their aggressiveness, inhibitors are used to reduce the rate of dissolution of metals. Compounds containing nitrogen, sulfur and oxygen are being used as inhibitors.² The most efficient inhibitors are organic compounds having π bonds in their structures. The efficacy of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface which consists of the replacement of water molecule at a corroding interface as



The adsorption of these compounds is influenced by the electronic structure of the inhibiting molecules^{3,4} and also by the steric factors, aromaticity, electron density at the donor atoms and also by the presence of functional groups such as =NH, —N=N—, —CHO, R—OH, R=R etc. in the inhibitor molecule.^{5,6} The role of molecular area⁷ and molecular weight⁸ of the organic molecule on its inhibi-

tion efficiency was also reported. Aniline and alkylamine⁹ *p*-substituted anilines¹⁰ are reported for its inhibition which is mainly due to the π electron interaction and the formation of co-ordination bond between Fe—N substituted anilines. In recent years, the conducting polymers¹¹ have attracted a great deal of attention for the research interest because of their excellent electrochemical properties, due to the presence of extensive delocalization of π electrons. These polymers are highly useful in electrochemical industries for the applications as sensor materials, rechargeable batteries, light emitting diodes, corrosion resistant coatings, electronic devices etc. More recently polymer amines^{12–21} were evaluated for their inhibition properties on the corrosion of iron and steel in acid solutions. In the earlier studies¹⁷ it has been found that polyaniline is able to inhibit corrosion of iron in H₂SO₄ solution. Since HCl is used as pickling solution in most of the cases, a study has been made on the inhibitive performance of polyaniline in HCl solution. In this work, the inhibitive behavior of poly(aniline) on iron in 1M HCl for different H⁺ and Cl⁻ ions has been studied using Impedance and polarization techniques.

EXPERIMENTAL

Preparation of poly(aniline)

Reagent grade Aniline was used for the preparation of water-soluble poly(aniline). A fresh 0.1M solution

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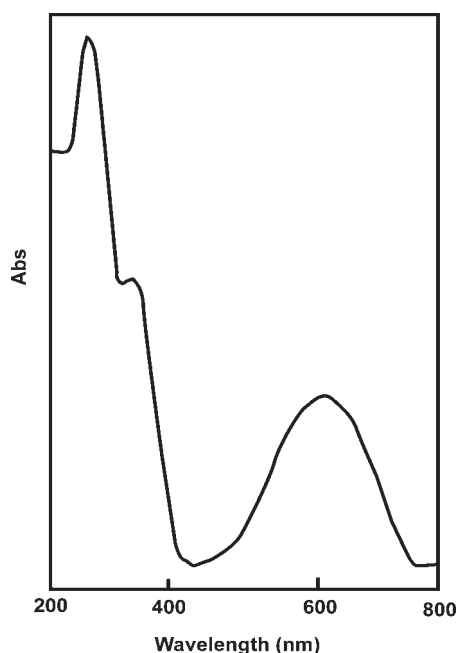


Figure 1 UV-visible spectrum for polyaniline.

of *p*-Toluene sulfonic acid was prepared using double distilled water. To this solution 0.1M of Aniline (in 0.1M HCl), was added and cooled to 0.5°C in a bath of ice and salt mixture. To this mixture, freshly prepared solution of Ammonium per sulfate (0.1M) was added slowly (to avoid warming) with constant stirring. The temperature was maintained below 5°C by the addition of crushed ice and stirring was continued for 2 h, to ensure the completion of reactions. The obtained polymer was characterized by FTIR and UV spectra, and the molecular weight determination was carried out by GPC method and was found to be 85,197.

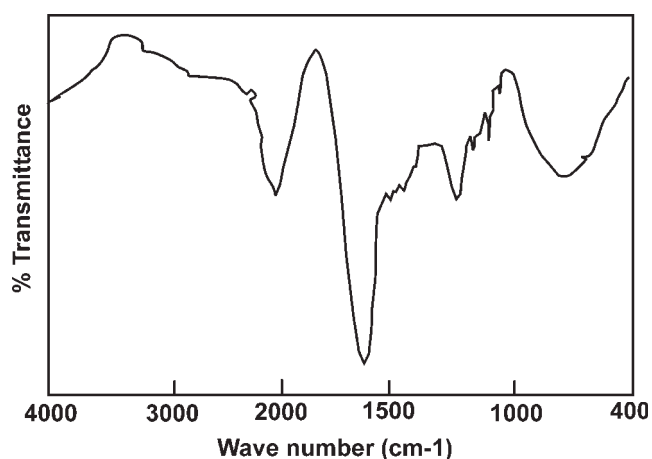


Figure 2 FTIR spectrum for polyaniline.

Evaluation of corrosion inhibition

Pure iron (99.998%) was used as a test electrode and it was embedded in Araldite, so as to expose the surface area of 1 cm². The electrode was polished successively with emery papers of grade 1/0, 2/0, 3/0, and 4/0, and then degreased with trichloroethylene. The electrochemical studies were carried out using a double walled glass cell of capacity 200 mL having provisions for the working electrode, counter platinum electrode and luggin capillary. The potential of the working electrode was measured with respect to saturated calomel electrode (SCE) through the luggin capillary. The experiments were carried out after the steady state attainment of corrosion potentials (15 m) at (30 ± 1)°C. All the solutions were prepared using reagent grade chemicals in double distilled water. The inhibitive effect of polyaniline in the concentration range of 50–500 ppm in 1M HCl was found out. Besides, the inhibitive performance of 500 ppm polyaniline in 1M–0.05M H⁺ concentration at 1M Cl⁻ concentration and 1M–0.1M Cl⁻ concentration at 0.1M H⁺ concentration was also studied.

The experiments were conducted using SOLARTRON Electrochemical Measurement Unit (1280B) with a software package of Z plot 2 and CORR WARE 2.

Impedance measurements were carried out at corrosion potential with an A.C. amplitude of 20 mV for the frequency range of 10 KHz to 10 mHz. The real and imaginary parts of the impedance were plotted in Nyquist plots. From the Nyquist plots, the diameter of the semicircle, the charge transfer resistance (R_{ct}) has been calculated using Zview software.

The inhibition efficiency of the inhibitor has been found out from the charge transfer resistance values using the following equation,

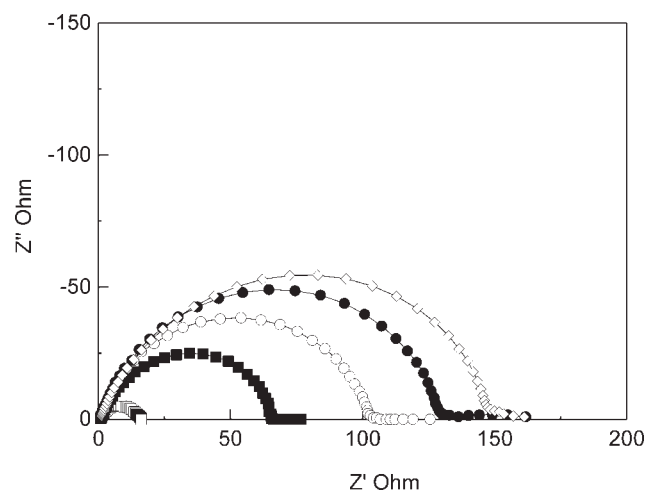


Figure 3 Nyquist plots of Iron in 1M HCl with different concentrations of Poly(aniline) □ Blank; ■ 50 ppm; ○ 100 ppm; ● 250 ppm; ◇ 500 ppm.

TABLE I
Impedance Parameters of Iron in 1M HCl without and with
Different Concentrations of Poly(aniline)

Poly(aniline) conc. (ppm)	Charge transfer resistance R_{ct} ($\Omega \text{ cm}^2$)	Double layer capacitance C_{dl} ($\mu\text{F}/\text{cm}^2$)	Inhibition efficiency % I.E.	Surface coverage (θ)
Nil	15.6	330.1	–	–
50	65.3	217.7	76.1	0.34
100	103.1	153.4	84.9	0.53
250	129.4	143.7	87.9	0.57
500	151.2	111.7	89.7	0.66

$$I.E.\% = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100$$

where R_{ct} and R'_{ct} are the charge transfer resistance values in the absence and presence of inhibitors.

The interfacial double layer capacitance (C_{dl}) value has been estimated from the impedance value of the frequency having maximum imaginary component (f_{max}) in the Nyquist plot by using the following equation,

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}}$$

and the surface coverage θ by the inhibitor molecule is given by

$$\theta = \frac{C_{dl} - C'_{dl}}{C_{dl} - C_{dls}} = \frac{C_{dl} - C'_{dl}}{C_{dl}}$$

(since $C_{dls} \ll C_{dl}$) where C_{dl} , C'_{dl} , and C_{dls} are the double layer capacitance values in the absence, presence of polyaniline inhibitors and saturated value in the presence of inhibitor respectively.^{22–24}

For linear polarization resistance studies, the measurements were carried out by scanning the potential in the range of -15 to $+15$ mV with respect to open circuit potential at the scan rate of 1mV/s . The E and i data were plotted in a linear scale to get LPR plots and the slope of the plot gave the polarization resistance (R_p). From the measured polarization resistance values, the inhibition efficiency has been calculated using the relationship,

$$I.E.\% = \frac{R'_p - R_p}{R'_p} \times 100$$

where R_p and R'_p are the polarization resistance values without and with the addition of inhibitors.

For potentiodynamic polarization studies, the experiments were carried out over a potential range of -200 mV to $+200$ mV with respect to open circuit potential at a scan rate of 1mV/s . The various kinetic parameters such as corrosion current (i_{corr}), an-

odic tafel slope (b_a) and cathodic tafel slope (b_c) have been obtained from the polarization curves.

The inhibition efficiency was evaluated from the measured i_{corr} values using the relationship

$$I.E.\% = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100$$

where i_{corr} and i'_{corr} are the corrosion current values without and with the addition of various concentrations of inhibitor.

RESULTS AND DISCUSSION

Characterization of synthesized polyaniline

The absorption peak at 260nm shows $\pi-\pi^*$ transition in the benzenoid ring and 620nm shows the donor-acceptor interaction of quinonoid ring. Cation radicals and localized polaron peaks were observed at 330nm ^{25,26} (Fig. 1). The major IR absorption bands (Fig. 2) around 1500cm^{-1} and 1600cm^{-1} are the characteristics band due to benzenoid ring structure and quinoid ring structure, respectively, and the

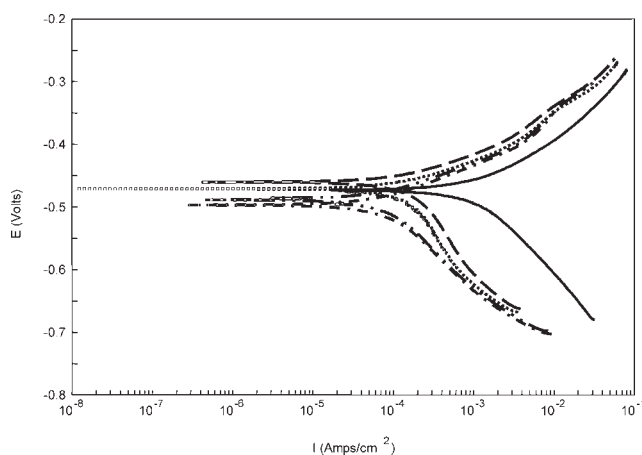
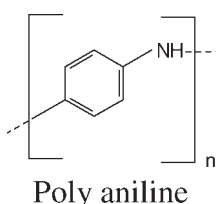


Figure 4 Polarisation plots of Iron in 1M HCl with different concentrations of Poly(aniline). — Blank; - - - 50 ppm; 100 ppm; - · - 250 ppm; — · — 500 ppm.

TABLE II
Electrochemical Parameters of Iron in 1M HCl without and with Different Concentrations of Poly(aniline)

Poly(aniline) Conc (ppm)	Tafel polarization method					LPR method	
	E_{corr} (mV)	b_a (mV)	b_c (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	I.E.%	R_p ($\Omega \text{ cm}^2$)	I.E.%
Nil	-488.4	89.7	123.1	1425.5	-	17.4	-
50	-461.1	84.3	122.4	275.7	80.6	78.1	77.7
100	-468.9	85.2	127.1	225.2	84.2	120.4	85.5
250	-498.6	80.3	123.5	118.3	91.6	184.6	90.5
500	-503.1	83.7	122.9	105.1	92.6	183.4	90.5

other characteristics peaks for poly aniline at, 1211 cm^{-1} , 1125 cm^{-1} are due to C-N, C-H bending.^{27,28} The structure of polyaniline would be



Inhibition of poly(aniline) in 1M HCl

The impedance behavior of Iron in 1M HCl without and with different concentrations of poly(aniline) in the concentration range 50–500 ppm is shown in Figure 3. The charge transfer resistance (R_{ct}) values, the double layer capacitance (C_{dl}) values, and surface coverage (θ) values calculated from the impedance diagrams are given in Table I. The R_{ct} values increase from 15.6 $\Omega \text{ cm}^2$ for inhibitor free solution

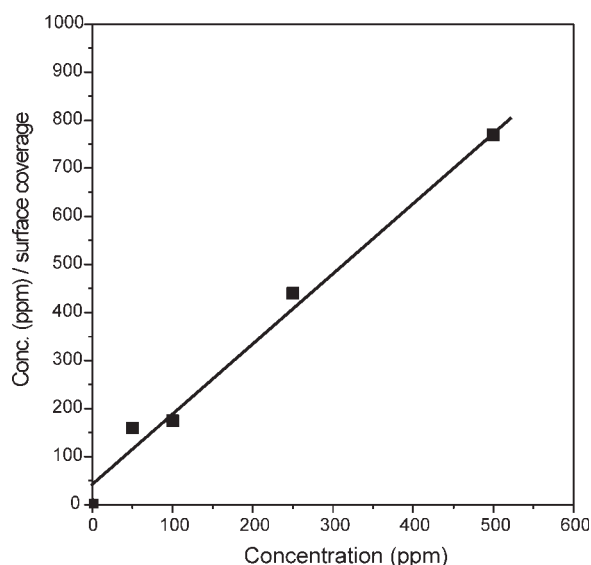


Figure 5 Langmuir isotherm plot for polyaniline.

to 151.2 $\Omega \text{ cm}^2$ for 500 ppm of polyaniline. The double layer capacitance decreases steadily from 330.1 $\mu\text{F cm}^{-2}$ for the blank acid to 111.7 $\mu\text{F cm}^{-2}$ for the maximum concentration of polyaniline.

The potentiodynamic polarization behavior of iron in 1M HCl without and with various concentrations of poly(aniline) is shown in Figure 4. The corrosion kinetic parameters obtained from these diagrams are given in Table II. It is found that, there is no significant variation in the E_{corr} values with the addition of inhibitors suggesting that this polymer behaved as a mixed type of inhibitor. The corrosion current density decreases from the blank value of 1425.5 to 105.1 $\mu\text{A cm}^{-2}$ for 500 ppm of polyaniline corresponding to 92.6% of corrosion inhibition. It is observed that, there is a steady increase of inhibitor efficiencies with the added inhibitor concentration as observed in the impedance results. The anodic tafel slopes are 85 ± 5 mV and the cathodic tafel slopes are 123 ± 3 mV. Since the tafel slopes are not markedly affected with the addition of ipolyaniline, it shows that the inhibitor inhibits by adsorption without affecting the mechanism of iron dissolution and hydrogen evolution.

The slope of the linear polarization curves, the polarization resistance R_p obtained from the LPR curves for iron in 1M HCl without and with polyaniline is also included in Table II. It is seen that the R_p

TABLE III
Impedance Parameters of Iron in Different H⁺ Ions Concentrations without and with 500 ppm Poly(aniline)

System	Conc. of [H ⁺]	Charge transfer resistance R_{ct} ($\Omega \text{ cm}^2$)	Double layer capacitance C_{dl} ($\mu\text{F}/\text{cm}^2$)	I.E.%
Blank	1.0M	15.6	330.1	-
	0.5M	81.4	215.0	-
	0.1M	92.9	146.8	-
	0.05M	109.3	123.8	-
Poly(aniline)	1.0M	151.2	117.7	89.7
	0.5M	164.4	108.7	50.5
	0.1M	168.2	101.5	44.8
	0.05M	176.9	97.8	38.2

TABLE IV
Impedance Parameters of Iron in 0.1M HCl for Different Cl⁻ Ions Concentrations without and with 500 ppm Poly(aniline)

System	Conc. of [Cl ⁻]	Charge transfer resistance R_{ct} (Ω cm ²)	Double layer capacitance C_{dl} (μ F/cm ²)	% I.E.
Blank	1.0M	92.9	146.8	-
	0.5M	107.1	134.1	-
	0.1M	127.0	124.5	-
Poly(aniline)	1.0M	168.2	101.5	44.8
	0.5M	190.8	98.6	43.8
	0.1M	216.1	92.0	41.2

increases from 17.4 Ω cm² for inhibitor free acid to 183.4 Ω cm² for the maximum concentration of poly-aniline studied yielding 90.5% of inhibition efficiency.

The adsorption character of inhibitor can be represented by adsorption isotherm. Figure 5 gives the plot of C_{inh} versus C_{inh}/θ . This isotherm plot shows that, the inhibitor obeys Langmuir's adsorption isotherm. The adsorption of inhibitor at a metal-solution interface can be represented as substitutional adsorption process between the inhibitor molecules in the aqueous solution and the water molecules on the metallic surface.²⁹ Earlier studies showed that, the inhibitive properties of poly(aniline) and substituted polyaniline for mild steel in sulfuric acid solutions^{17,18} are very effective, due to the presence of π electrons, quaternary nitrogen atom and the larger molecular size which ensures greater coverage of the metallic surface.

The inhibitive property of poly(aniline) is also due to the presence of π electrons, quaternary nitrogen atom and the larger molecular size which ensures greater coverage of the metallic surface. The adsorption of polymer amine molecules on the metal surface can be either electrostatic adsorption of cationic form of polymer with iron atoms (or) the adsorption occurs through π electrons interaction with the metal surface.

Inhibition of poly(aniline) for various concentrations of H⁺ and Cl⁻ ions

The impedance and polarization measurements for iron in 0.05–1M [H⁺] ions concentrations and 0.1–1M for [Cl⁻] ions concentrations, were conducted without and with 500 ppm poly(aniline). The charge transfer resistance (R_{ct}) values, and the double layer capacitance (C_{dl}) values, calculated from the impedance studies are given in Tables III and IV. The electrochemical parameters obtained from polarization experiments are given, in Tables V and VI, respectively.

In the case of H⁺ ions concentrations, it is observed that, the inhibitor efficiency is found to decrease with H⁺ ions concentration. This may be due to the decrease in the concentration of cationic formation of poly(aniline). Amines in aqueous acidic solutions may exist as either neutral molecules or in the form of cations depending on the concentration of H⁺ ions in the solutions.³⁰ In higher concentration of H⁺ ions solutions they predominantly exist as cations and adsorb through electrostatic interaction between the positively charged anilinium cation and negatively charged metal surface. The stronger adsorption of the organic amine molecules with the metal surface is found at high concentration of H⁺ ions.^{31,32}

Further it is found that, at higher Cl⁻ ions concentration, the inhibitive effect of poly(aniline) is promoted. For the aromatic amines, the Cl⁻ ions, which are preferentially adsorbed on the iron electrode surface and makes the surface more negative.³³ Therefore, Cl⁻ ions enhance the adsorption of aromatic amines and improve the inhibitive effect to a considerable extent.^{21–26}

CONCLUSIONS

Polyaniline is found to be an efficient corrosion inhibitor for iron in HCl solution. The adsorption of polyaniline is found to obey Langmuir adsorption isotherm. The inhibitor performance of polyaniline is

TABLE V
Electrochemical Parameters of Iron in Different H⁺ Ions Concentrations without and with 500 ppm Poly(aniline)

System	Conc (H ⁺)	Tafel polarization method				LPR method		
		E_{corr} (mV)	b_a (mV)	b_c (mV)	I_{corr} (μ A/cm ²)	I.E.%	R_p (Ω cm ²)	I.E.%
Blank	1.0M	-488.4	89.7	123.1	1425.5	-	17.4	-
	0.5M	-511.8	89.6	100.9	185.4	-	119.9	-
	0.1M	-548.5	84.5	102.7	158.2	-	126.7	-
	0.05M	-559.2	86.4	116.2	140.0	-	153.9	-
Poly(aniline)	1.0M	-503.1	83.7	122.9	105.1	95.6	183.4	90.5
	0.5M	-513.3	89.9	104.9	67.2	63.8	200.7	40.3
	0.1M	-516.3	84.7	104.5	62.9	60.2	209.6	39.6
	0.05M	-532.2	82.1	100.0	56.2	59.9	238.2	35.4

TABLE VI
Electrochemical Parameters of Iron in 0.1M HCl for Different Cl⁻ Ions Concentrations
without and with 500 ppm Poly(aniline)

System	Conc (Cl ⁻)	Tafel polarization method					LPR method	
		E_{corr} (mV)	b_a (mV)	b_c (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	I.E.%	R_p ($\Omega \text{ cm}^2$)	I.E.%
Blank	1.0M	-548.5	84.5	102.7	158.2	-	126.7	-
	0.5M	-535.5	83.7	111.7	140.1	-	152.9	-
	0.1M	-522.2	89.6	105.8	131.7	-	158.3	-
Poly(aniline)	1.0M	-516.3	84.7	104.5	62.9	60.2	209.6	39.6
	0.5M	-508.5	88.0	103.2	57.7	58.8	224.9	32.0
	0.1M	-503.5	81.0	104.5	55.3	58.0	230.2	31.2

found to be dependent on the H⁺ and Cl⁻ ions concentration. The inhibition of polyaniline is found to be more effective at higher H⁺ and Cl⁻ ion concentration.

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